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Evaluation of cobalt oxides for calcium battery cathode applications

A. Torres[a], F. Bardé[b], M.E. Arroyo-de Dompablo[a,*]

[a] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain
[b] Toyota Motor Europe, Research & Development, Advanced Material Research, Battery & FC, Technical Centre, Hoge Wei 33 B, B-1930 Zaventem, Belgium

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ABSTRACT

The identification of potential cathode materials is a requirement for the development of a rechargeable calcium based battery technology. In this work, we use Density Functional Theory (DFT) calculations to explore the electrode characteristics of three ternary calcium cobalt oxides with distinct Co—O dimensionality: 3D-$Ca_2Co_2O_5$ (brownmillerite type structure), 2D-$Ca_3Co_4O_9$ (a misfit compound) and 1D-$Ca_3Co_2O_6$ (K_4CdCl_6 structural type). For the three compounds calculations predict Co^{3+}/Co^{4+} voltages in the 3–4 V range, with a volume variation below 8% upon Ca deinsertion. Further Co^{4+} oxidation is predicted at too high voltages not reachable in practice. The maximum specific capacities are therefore 192 mAh/g ($Ca_2Co_2O_5$), 165 mAh/g ($Ca_3Co_4O_9$) and 160 mAh/g ($Ca_3Co_2O_6$). The potential application of $Ca_2Co_2O_5$ is discarded based on a large energy barrier for Ca diffusion (1.3 eV). With energy barriers for Ca diffusion of 0.9 eV, the 2D and 1D oxides are appealing as low rate cathode materials. To complete a previous experimental investigation, we have analyzed the reversibility of the Ca deinterclation reaction of 1D-$Ca_3Co_2O_6$. It is found that a phase transformation takes place upon decalciation driven by the change in the electronic configuration of Co ions (from High Spin-trigonal prismatic Co^{3+} to octahedral Low Spin-Co^{4+}) and involving the Ca diffusion pathways.

1. Introduction

Lithium-ion batteries (LIB) are a key component for portable electronic devices, more importantly, they may offer a possible near-term solution for environment-friendly transportation and energy storage for renewable energies source such as solar and wind. Although LIB offer higher energy density and a longer cycle life than other battery technologies, to meet the increasing energy and power demand at lower cost, advances in electrochemical energy storage systems are urgently needed. An attractive longer term alternative is to combine sustainability with prospects of high energy density and develop metal anode technologies based on multivalent abundant elements such as Ca or Mg [1]. Calcium is an attractive candidate due to its low cost, natural abundance and low reduction potential [2–4]. At this very early stage of the Ca-based technology, critical technical advancements are necessary towards overcoming the existing hurdles [5]. Among them, developing cathode materials enabling effective diffusion of Ca^{2+} ions is far from being evident [6]. Several compounds (oxides, sulphides and phosphates) have been investigated as cathode intercalation materials for Ca batteries. Recent reviews summarize the main results [2,4,5]. A specific capacity around 200 mAh/g at 2 V is attainable for the classical intercalation material TiS_2 [7], with other chalcogenides offering interesting prospects in terms of Ca diffusion although with a penalty in voltage [8,9]. The more sluggish kinetics of Ca^{2+} diffusion in oxides is a handicap to develop high energy density cathode materials [4,10–12]. The local topology is a critical factor for Ca^{2+} mobility [6,10,12], and fundamental research is needed to identify propitious crystal chemistries.

The high redox potential of the Co^{4+}/Co^{3+} couple makes cobalt oxides an interesting class of materials to investigate. In addition, calcium cobalt oxides crystallize in a variety of structural types, allowing to map fundamental cathode properties-structure relationship. Preliminary work suggests reversible electrochemical activity for layered-$CaCo_2O_4$ (a form without stability field in the P-T Ca-Co-O phase diagram) in electrochemical cells bearing V_2O_5 as the anode [13]. Irreversible calcium extraction has been proven for $Ca_3Co_2O_6$ at 3.5 V vs the Ca electrode [14]. In addition good electrochemical properties are predicted for the virtual spinel $CaCo_2O_4$ [15]. These promising results encourage the investigation of other calcium cobalt oxides. Two ternary oxides appear in the CaO-CoO phase diagram: $Ca_3Co_2O_6$ and $Ca_9Co_{12}O_{28}$ (normally expressed as $Ca_3Co_4O_9$) [16–18]. Another ternary oxide with the brownmillerite structure ($Ca_2Co_2O_5$) has been reported [19,20]. From the crystal dimensionality point of view, the Co—O arrangements in these oxides provide a 3D (brownmillerite), 2D

* Corresponding author.
E-mail address: e.arroyo@quim.ucm.es (M.E. Arroyo-de Dompablo).

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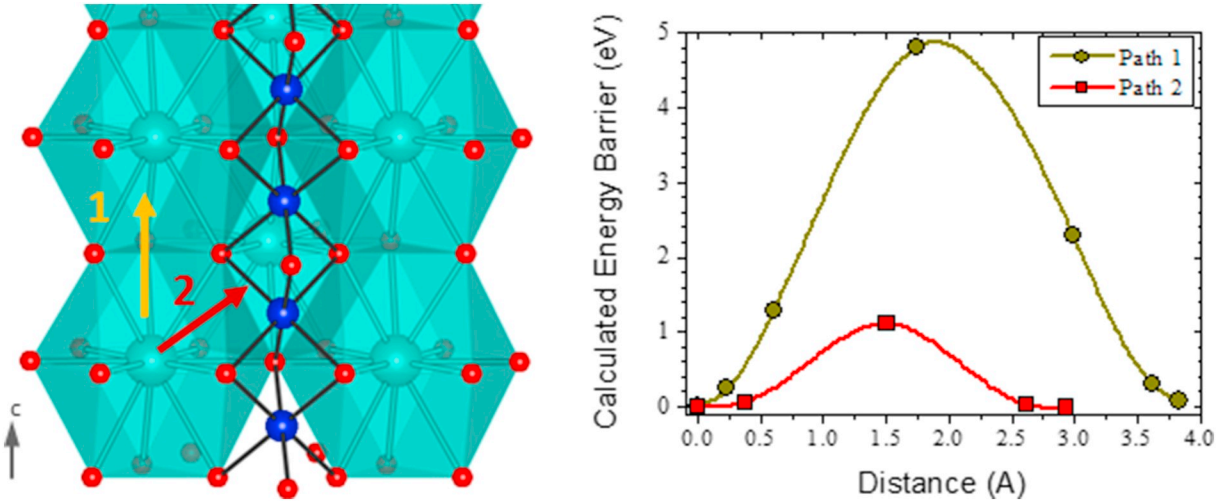

Fig. 7. Ca diffusion pathways and respective calculated energy barriers for the $BaCoO_3$-like $Ca_2Co_2O_6$ structure. A supercell $Ca_{23}Co_{24}O_{72}$ is used in the calculations. Color code: Ca light blue, Co dark blue, O red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

characteristics for Ca-based batteries. For the three materials, the Co^{3+}/Co^{4+} redox couple falls in the 3–4 voltage window, being compatible with the known electrolytes. A positive finding is the low volume variation associated to the Ca deinsertion reactions (below 8%). The calculated energy barriers for Ca^{2+} migration (1.3 eV for the 3D, and 0.9 eV for both the 2D and 1D oxides) are indicative of a hampered Ca diffusivity in these materials. Despite these barriers are considerably lower than the reported for other oxides, they are still too high as to permit a good Ca diffusion, thereby impeding a fast kinetics for the deintercalation reaction. Yet, some electrochemical activity might be expected at low rates, as experimentally confirmed for $Ca_3Co_2O_6$ at C/200 rate [7]. In that line, 2D-$Ca_3Co_4O_9$ is other interesting material for further experimental and computational investigations.

Unsurprisingly, average insertion voltages, volume variation and theoretical specific capacities are not correlated with the lattice dimensionality. Regarding diffusion, layered (2D) materials are attractive as Ca-cathodes since the expandable interlayer space might facilitate Ca^{2+} intercalation. Yet, we found no evidence to expect a superior cathode performance for 1D/2D structures, at least for the present case where the deliverable specific capacity is determined by the redox couple, and some Ca ions will unavoidably remain in the decalciated-phases. Excluding the potential benefit of an empty interlayer/interchain space expansion, our results support that the local topology rather than the dimensionality is the main factor in Ca diffusion.

The reversibility of the Ca intercalation reactions is a major concern already remarked in the experimental investigations of $CaSi_2$ [60], TiS_2 [7], MoO_3 [61] and $Ca_3Co_2O_6$ [14]. The four materials display electrochemical activity, associated to Ca extraction or insertion, but with the common feature of a poor or negligible reversibility. Advances in experimental protocols and set-up are mandatory to discern whether irreversibility obeys to inherent properties of the cathode materials, or to issues related to the electrolyte and interfaces. In the case of 1D-$Ca_3Co_2O_6$, the present investigation discloses that Ca-deintercalation drastically modifies the electronic/crystal structures as well as the existing Ca-diffusion pathways. This phase transformation upon Ca deinsertion (Co^{3+} oxidation) may compromise the reversible capacity of $Ca_3Co_2O_6$ as cathode material.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ssi.2019.115004.

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